

REMARKS

Favorable reconsideration and allowance of the claims presented herein are respectfully requested.

Claims 1-13 are pending in this application.

In the Office Action, the Examiner has objected to the disclosure for improperly referring to the present application as a continuation of prior application Serial No. 08/831,828, filed March 16, 1995. The Examiner alleges that in order to qualify as a continuation, the disclosure presented in the second application must be the same as that of the original application (M.P.E.P. § 201.07) [Examiner's emphasis]. Thus, it is the Examiner's belief that while pages 6-11 of the present application appear to be identical to the corresponding pages in prior application Serial No. 08/381,828, pages 1-5 of the present application are significantly different from the corresponding pages in prior application Serial No. 08/381,828.

Applicants respectfully submit that the present application is a proper continuation application of prior application Serial No. 08/381,828, filed March 16, 1995, claiming priority to European publication WO 94/03249, filed July 29, 1993, which claims priority to NL 9201418, filed August 7, 1992 as pages 1-5 of the present application are the same as the corresponding pages in prior application Serial No. 08/381,828 as filed. This can be shown in prior application Serial No. 08/831,828 (the parent application of the present application) where a complete filing of the application under 35 U.S.C. §371 was made on February 16, 1995. When filing the parent application, a copy of the published WO 94/03249 (Exhibit I) , together with a copy of the International Preliminary Examination Report (Exhibit II) was included in the §371 filing. Also included in the §371 filing was PTO Form

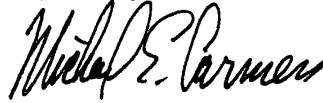
1390 which indicated that the International application as filed was being transmitted by the International Bureau (Exhibit III). In addition, applicants received a Notification of Acceptance of Application Under 35 U.S.C. § 371 mailed April 11, 1995 (Form PCT/DO/EO903) showing that a copy of the International application was received by The United States Patent and Trademark Office (Exhibit IV). A comparison of pages 1-5 of WO 94/03249 as filed in parent application Serial No. 08/831,828 to pages 1-5 of the present application clearly shows that pages 1-5 of WO 94/03249 are identical to pages 1-5 of the present application. Therefore, no new matter has been added to the present application and the present application is a proper continuation application of prior application Serial No. 08/831,828. Accordingly, withdrawal of the objection is warranted and such is respectfully requested.

The Examiner has rejected Claims 1-13 under 35 U.S.C. § 102(b) as being anticipated by WO 94/03249. As stated above, the subject application is a proper continuation application of prior application Serial No. 08/831,828. As such, the present application is entitled to the chain of priority which includes WO 94/03249. Accordingly, as WO 94/03249 is in the chain of priority, the rejection under 35 U.S.C. § 102(b) is deemed moot. Therefore, withdrawal of the rejection is respectfully requested.

Also in the Office Action, the Examiner has objected to the disclosure for certain informalities and required correction of the informalities. The disclosure has been corrected so there are no existing informalities. Accordingly, withdrawal of the objection is respectfully requested.

For the foregoing reasons, Claims 1-13 as presented herein are believed to be in condition for allowance. Early and favorable action is earnestly solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Michael E. Carmen". The signature is fluid and cursive, with the first name "Michael" and last name "Carmen" being clearly legible.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B01D 15/00, C02F 1/28	A1	(11) International Publication Number: WO 94/03249 (43) International Publication Date: 17 February 1994 (17.02.94)
(21) International Application Number: PCT/EP93/02029 (22) International Filing Date: 29 July 1993 (29.07.93) (30) Priority data: 9201418 7 August 1992 (07.08.92) NL (71) Applicant (for all designated States except US): AKZO N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): BUIJTENHUIJS, Frederik, Albert [NL/NL]; Drentesingel 131, NL-6835 HM Arnhem (NL). PRAGT, Johanne, Josef [NL/NL]; Iepen- hof 14, NL-6951 MG Dieren (NL). SCHOMAKER, Elwin [NL/NL]; Tuinstraat 2, NL-6882 NX Velp (NL).	(74) Agent: SCHALKWIJK, P. C.: Akzo N.V., Patent Department (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL). (81) Designated States: AU, CA, CZ, FI, HU, JP, KR, NO, PL, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	
(54) Title: MATERIAL FOR EXTRACTING HYDROPHOBIC COMPONENTS DISSOLVED IN WATER (57) Abstract Use of a porous, preferably dimensionally stable, material for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, the material containing a hydrophobic substance exhibiting great affinity for the constituents to be extracted from the water, characterised in that the material has a surface which will be wetted more readily by the hydrophobic substance immobilised in the pores having an average diameter in the range of 0.1 to 50 µm than by the aqueous solution, with the proviso that at least 60 % of this substance can be extracted from the pores by a liquid wholly made up of the constituents to be extracted.		

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MATERIAL FOR EXTRACTING HYDROPHOBIC COMPONENTS DISSOLVED IN WATER

5 The invention relates to the use of a porous, preferably dimensionally stable, material for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, the material containing a hydrophobic substance exhibiting great affinity for the constituents to be extracted from the water.

10 Such a use, with a porous material being employed, was earlier described in GB-A-1 535 481. The porous material employed in this document consists of mineral carriers which are inert with respect to water, to the hydrophobic substance to be used as extractant, and to the compound to be extracted. Examples of suitable mineral carriers mentioned are pumice, kieselguhr, bauxite, alumina, carbon, or
15 silicates. The particles preferably have a size in the range of 0,1 mm to 5 cm. It is stated that the pore size is critical only to the extent that it should be large enough to permit penetration of the compound to be extracted, of the extraction solvent, and of the regeneration liquid.

20 In actual practice, using the known materials for the aforementioned extraction process is attended with major drawbacks because the hydrophobic substances absorbed in them are easily displaced by water, especially when a packed bed is employed. In consequence, the water to be extracted or purified is in fact contaminated rather than
25 decontaminated by these substances.

The invention now provides for the use of a porous material with a hydrophobic substance absorbed therein which, a significant increase
30 in the capacity per volume unit notwithstanding, does not give rise to stability problems, not even when utilised on an industrial scale.

5 The invention consists in that when a porous material of the known type mentioned in the opening paragraph is used, it has a surface which will be wetted more readily by the hydrophobic substance immobilised in the pores of an average diameter in the range of 0,1 to 50 μm than by the aqueous solution, with the proviso that at least 60% of the hydrophobic substance can be extracted from the pores by a liquid wholly made up of the constituents to be extracted.

10 To determine the average pore diameter advantageous use is made of mercury porosimetry in accordance with ASTM D 4248-83.

15 According to the invention, preference is given to the use of a porous material at least 85% of which can be extracted from the pores by a liquid wholly composed of the constituents to be extracted.

20 It is to be considered extremely surprising that by the use of a porous material having a hydrophobic surface as well as an average pore diameter within the given range both the stability and the extraction capacity are so enhanced that now, for the first time, application on an industrial scale has become feasible.

25 It was found that, in general, optimum results can be obtained when using a material having an average pore diameter in the range of 0,2 to 15 μm .

30 The hydrophobic immobilised material may be solid matter as well as a liquid. If the immobilised material is a solid, preference is given to a polymer which swells in the hydrophobic substance to be extracted. Examples of polymers which are suitable for use within the framework of the invention include polymethyl(meth)acrylate, styrene-acrylonitrile copolymer, and acrylonitrile-butadiene-styrene copolymer, all of which may be partially cross-linked or not. Preference is given in this case to polystyrene. If the immobilised

material is a liquid, use is made of a liquid having the greatest possible affinity for the hydrophobic constituents to be extracted. Needless to say, this liquid should be virtually insoluble in the aqueous solution to be extracted and be so immobilised in the porous material that it cannot flow from the porous structure.

5 Within the framework of the invention preference is given to the use of a liquid in the form of a glycerol ester of one or more, preferably unsaturated, fatty acids.

10 In general, favourable results are attained if the immobilised liquid is an oil, such as palmitic oil, olive oil, peanut oil, paraffinic oil, fish oil such as herring oil, linseed oil, and, in particular, soybean oil and/or castor oil.

15 Generally, favourable results are attained when using a material of which at least 15 vol.% of the pores is filled with the substance immobilised therein, with optimum results being obtained using a material of which at least 50 vol.% and not more than 95 vol.% of the pores is filled with the substance immobilised therein. Completely-filled up pores may cause problems on account of swelling (solid matter) or expansion (liquid), which may lead to the dimensions of the porous material being interfered with or to the immobilised liquid bursting the pores. In the case of porous materials wholly filled up with a liquid hydrophobic substance being used, these difficulties can easily be overcome by mixing the filled material with unfilled (porous) material, so that the generated excess can be absorbed during extraction. Alternatively, when a packed bed is used, the unfilled (porous) material may be deposited at the two ends of the bed as separate boundary layers. When these types of steps are taken, 100 vol.-%-filled materials may also be employed.

30 The porous material preferably is organic in origin. However, it is also possible to use a porous inorganic material, providing it has a hydrophobic surface, e.g., through the application of a coating.

Within the framework of the invention preference is given to the use of natural and synthetic organic materials, the latter materials being preferred for reasons of reproducibility. Examples of synthetic organic materials include porous polymers, more particularly those of which the preparation is disclosed in US Patent Specification 4 247 498.

Examples of polymers deemed more or less suitable for use in the present invention include:

low pressure polyethylene, high pressure polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene terpolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(4-methyl-pentene-1), and polybutene.

Optimum results were attained by employing polyolefin based polymers, with preference being given to the use of a polypropylene based porous material.

The porous polymer is generally used in the form of grains having an average particle diameter of 0,1 to 10 mm. Alternatively, the polymer may be employed in the granulated form, as well as in the form of membranes, fibres which may be hollow or not, etc.

When in the form of a granulate or a powder, the porous polymer may be used in a packed bed, a fluidised bed, or a tank with stirring. Fibres which may be hollow or not are used in the form of fabrics and non-wovens, respectively.

Particularly when a glycerol ester of one or more unsaturated fatty acids is employed to extract aromatic compounds from aqueous solutions, preference is given to a porous material obtained by a process such as described in DE-A-32 05 289. By this process a structure may be obtained which has pores of an average diameter in the range of 0,1 to 50 μm . Especially favourable results may be

obtained when using polypropylene as porous material and soybean oil/castor oil as hydrophobic substance.

Needless to say, the materials according to the invention are not just suitable for extracting aromatic waste matter from aqueous solutions; extracting useful constituents such as biologically active constituents from usually highly dilute aqueous solutions is also within the bounds of possibility.

Generally, the procedure used to prepare the extracting material according to the invention is as follows: first, 5-90 wt.% of a polymer is dissolved, with heating, at a temperature above the upper critical decomposition temperature T_c in 10-95 wt.% of a mixture of two liquid and miscible compounds A and B, the mixing ratio of A to B being so selected as to give decomposition on cooling, resulting in a polymer-rich and a polymer-poor phase. On further lowering of the temperature this decomposition structure is then fixed prior to the completion of the phase separation, due to vitrification or crystallisation of the polymer, resulting in a porous polymer material filled with the mixture of compounds A and B which is pre-eminently suited to be used within the framework of the invention, either as such or after diminution if so desired.

The invention will be illustrated with reference to the following examples, which, of course, are not to be construed as limiting in any manner the scope of the invention.

Example I

A glass column of 2 m in length and with a diameter of 23 cm, which at its top and bottom was closed up with perforated screens having apertures of 1 mm in diameter, was filled over a length of 180 cm with a porous polypropylene powder filled with oil (hydrophobic extractant).

Two experiments were carried out, the first one making use of polypropylene powder partially filled with soybean oil, the second one employing polypropylene powder wholly filled with soybean/castor oil. The two powders also differed from each other in terms of particle size distribution.

The powders in question had the following specifications:

	Powder I	Powder II
particle diameter	350 - 1000 μm	100 - 2000 μm
porosity	3 ml/g	3 ml/g
average pore diameter	10 μm	10 μm
degree of substitution with oil	60 wt.%	72 wt.%

In order to prevent the fine polypropylene powder from clogging up the apertures of the perforated screens, in each of the two arrangements the powder was bounded on either side by a 10 cm thick layer of the same material in the form of unfilled granules of 3-4 mm in diameter.

Powder I (7,38 kg) was filled with 11,06 kg of soybean oil to give a total of 18,44 kg.

Powder II (8,04 kg) was filled with 20,51 kg of soybean oil/castor oil to give a total of 28,55 kg.

The rate of flow of the liquid was 157 l per hour at a temperature of 24°C. The average overall aromatics content in the water to be purified was 840 ppm, the benzene content was 630 ppm, the toluene content 60 ppm.

In the case of powder I, the aromatics concentration in the effluent during an extraction process lasting well over 12 hours could not be measured. By then, the material had absorbed about 6,5 wt.% of benzene and 8,5 wt.% of aromatics, respectively.

5 In the case of powder II, the aromatics concentration in the effluent during an extraction process lasting well over 20 hours could not be measured. By then, the material had absorbed about 7 wt.% of benzene and 9 wt.% of aromatics, respectively. The point of saturation was
10 reached after about 45 hours, when more than 15 wt.% of aromatics had been absorbed.

The aromatics content was measured intermittently by IR spectroscopy in accordance with ASTM D3921-85, the benzene content by liquid
15 chromatography.

Example II

The column of Example I was now filled with 28,3 kg of powder II, which was bounded on either side by a 5-10 cm thick layer of unfilled
20 polypropylene granules. The rate of flow of the liquid was 300 l per hour at a temperature in the range of 11° to 13°C. The water to be treated had the following influent concentrations:

chloroform	0,5 ppm
carbon tetrachloride	32 ppm

25 After 4 hours in the loaded state, with the contaminated water flowing upwards from the bottom, the column was regenerated with 103°C steam for 4 hours, with the steam being passed through the column in opposite direction to the water. The rate of flow of the steam was
30 4 kg per hour. The subsequent periods of loading also were 4 hours each. After eleven of such loadings the efficiency of the column continued unchanged. The effluent concentrations of the treated water were measured by means of gas chromatography using an electron capture

detector (ECD) and found to be below the detection limit for chloroform and carbon tetrachloride of < 10 ppb (parts per billion), except that in the case of carbon tetrachloride values < 60 ppb were measured occasionally.

5 After condensation of the steam, the chloroform and carbon tetrachloride were drawn off from a liquid separator as lower layer.

Example III

10 In a manner analogous to that disclosed in Example I, two glass columns of 2 m in length and 23 cm in diameter were installed. These columns likewise were closed up at the top and the bottom with perforated screens having apertures of 1 mm in diameter. In order to achieve better distribution over the columns of the powder to be introduced, the columns were filled with stainless steel Pall® rings
15 of 15 mm in diameter before being filled over a length of 190 cm with porous powder completely filled up with soybean/castor oil. In order to prevent clogging up of the perforated screens, the powder was bounded on either side by a 5-10 cm thick layer of identical material
20 in the form of unfilled granules having a diameter of 3-4 mm. The specification of the powder was as follows:

particle diameter	350-1000 μm
porosity	3 ml/g
average pore diameter	10 μm
degree of substitution	
25 with oil	72 wt.%

The amounts of powder differed per column: column 1 held 24,4 kg and column 2 29,4 kg.

30 The columns were loaded alternately, with the water to be treated being pumped from the bottom upwards and regeneration with 105°C atmospheric steam taking place from the top downwards. The rate of flow of the steam was 4 kg per hour.

After 32 loadings and regenerations the efficiency of the columns

proved unchanged.

The rate of flow of the liquid was 150 l per hour at a temperature of 6° to 13°C. The water to be treated had the following influent concentrations:

5	dichloromethane	195 ppm
	chloroform	39 ppm
	dichloroethane	32 ppm
	benzene	272 ppm
	toluene	137 ppm

10 The effluent concentrations were measured by means of gas chromatography using an electron capture detector (for chlorinated hydrocarbons) and flame ionisation (for benzene and toluene), respectively, and found to be below the detection limits for
15 chloroform, dichloroethane, benzene, and toluene of 10 ppb (for chloroform and dichloroethane) and 1 ppb (for benzene and toluene), respectively. The value measured for dichloromethane each time was < 0,6 ppm.

20 Example IV

In a manner analogous to that disclosed in Example III, two columns
25 were filled with Pall[®] rings, which this time had a diameter of 25 mm and were made of polypropylene. The columns were filled over a length of 180-190 cm, column 1 being filled with 28,3 kg of powder and column 2 with 23,8 kg. In order to prevent clogging up of the perforated screens, the powder was bounded on either side by a 5-10 cm thick
30 layer of unfilled polypropylene granules having a diameter of 3-4 mm. The regeneration was carried out at a rate of flow of the steam of 2 kg per hour. After 11 loadings and regenerations the efficiency of the columns proved unchanged.

The rate of flow of the liquid was 150 l per hour at a temperature of 15° to 20°C. The water to be treated had the following influent

concentrations:

1,1-dichloroethane	2-3 ppm
cis-1,2-dichloroethene	30-50 ppm
1,1,1-trichloroethane	1-8 ppm
trichloroethene	0,1-0,3 ppm

Again, the effluent concentrations were measured by means of gas chromatography using ECD and found to be below the detection limits for said solvents, which were as follows:

1,1-dichloroethane	< 50 ppb
cis-1,2-dichloroethene	< 150 ppb
1,1,1-trichloroethane	< 1 ppb
trichloroethene	< 1 ppb

After condensation of the steam the organic substances were drawn off from a liquid separator as lower layer.

Example V

In a manner analogous to that disclosed in Example IV, two columns were filled with Pall[®] polypropylene rings of 25 mm in diameter. Next, the columns were filled, over a length of 170 cm, with porous unfilled polypropylene powder. In order to prevent clogging up of the perforated screens, the powder was bounded on either side by a 10-20 cm thick layer of unfilled polypropylene granules having a diameter of 3-4 mm.

The specification of the powder was as follows:

particle diameter	350-1000 μ m
porosity	3 ml/g
average pore diameter	10 μ m
degree of substitution	
with oil	0 wt.%

Column 1 contained 7,22 kg of unfilled powder, column 2 held 7,26 kg.

First, xylene was passed through the columns until the pores were wholly filled with xylene and there was xylene sticking to the powder particles.

Next, there was alternate loading of the columns, with the water to be treated again being pumped through the column from the bottom upwards. The regenerant used was xylene of 20° to 50°C, which was passed through the column from the top downwards. The rate of flow of the xylene was 55 l per hour. After being regenerated, the columns were emptied with nitrogen, with the powder retaining 30 kg of xylene as extractant.

The rate of flow of the waste water to be treated was 150 l per hour at a temperature of 20° to 50°C.

The water to be treated had the following influent concentrations:

	o-cresol	70 - 250 ppm
	2-methyl-4-chlorophenoxyacetic acid	50 - 160 ppm
15	2,4-dichlorophenoxyacetic acid	1 - 20 ppm
	6-chloro-o-cresol	50 - 200 ppm
	4-chloro-o-cresol	90 - 200 ppm
	2-(2,4-dichlorophenoxy)propionic acid	4 - 7 ppm
20	2-(2-methyl-4-chlorophenoxy)propionic acid	3 - 13 ppm
	4,6-dichloro-o-cresol	7 - 16 ppm

Measurement of the effluent concentrations this time was by means of liquid chromatography using UV detection. The two columns had the same effluent compositions, with the measured concentrations always being lower than the following values:

	o-cresol	< 1 ppm
	2-methyl-4-chlorophenoxyacetic acid	< 1 ppm
	2,4-dichlorophenoxyacetic acid	<0,4 ppm
	6-chloro-o-cresol	<0,5 ppm
30	4-chloro-o-cresol	<0,5 ppm
	2-(2,4-dichlorophenoxy)propionic acid	<0,2 ppm
	2-(2-methyl-4-chlorophenoxy)propionic acid	<0,2 ppm
	4,6-dichloro-o-cresol	<0,1 ppm

CLAIMS

- 5 1. Use of a porous, preferably dimensionally stable, material for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, the material containing a hydrophobic substance exhibiting great affinity for the constituents to be
10 extracted from the water, characterised in that the material has a surface which will be wetted more readily by the hydrophobic substance immobilised in the pores having an average diameter in the range of 0,1 to 50 μm than by the aqueous solution, with the proviso that at least 60% of this
15 substance can be extracted from the pores by a liquid wholly made up of the constituents to be extracted.
2. Use according to claim 1, characterised in that the average pore diameter is in the range of 0,2 to 15 μm .
- 20 3. Use according to claim 1, characterised in that at least 85% of the immobilised hydrophobic substance can be extracted from the pores by a liquid wholly made up of the constituents to be extracted.
- 25 4. Use according to claim 1, characterised in that at least 15 vol.% of the pores is filled with the substance immobilised therein.
- 30 5. Use according to one or more of the preceding claims, characterised in that the immobilised substance is a polymer which swells in the hydrophobic substance to be extracted.

6. Use according to one or more of claims 1-4, characterised in that the immobilised substance is polystyrene.
7. Use according to claim 1, characterised in that the immobilised substance is a liquid.
8. Use according to claim 1, characterised in that the immobilised substance is a glycerol ester of one or more, preferably unsaturated, fatty acids.
9. Use according to claim 8, characterised in that the immobilised glycerol ester is soybean oil and/or castor oil.
10. Use according to claim 1, characterised in that the porous material is a polyolefin.
11. Use according to claim 10, characterised in that the porous material is polypropylene.
12. Use according to claim 1, characterised in that the porous material is obtained by the dissolving of a polymer in a solvent with heating, the cooling of the solution, and the mechanical diminution of the solidified mass if so desired.
13. Use according to claim 12, characterised in that the polymer is polypropylene and the solvent is soybean oil and/or castor oil.

ABSTRACT

5 Use of a porous, preferably dimensionally stable, material for the
extraction of hydrophobic constituents, such as benzene, toluene,
xylene and/or chlorinated hydrocarbons, from an aqueous solution, the
material containing a hydrophobic substance exhibiting great affinity
for the constituents to be extracted from the water, characterised in
10 that the material has a surface which will be wetted more readily by
the hydrophobic substance immobilised in the pores having an average
diameter in the range of 0,1 to 50 μm than by the aqueous solution,
with the proviso that at least 60% of this substance can be extracted
from the pores by a liquid wholly made up of the constituents to be
15 extracted.

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INTERNATIONAL SEARCH REPORT

International Application No.

P. /EP 93/02029

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B01D15/00 C02F1/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NL,A,7 701 328 (IFP) 15 August 1977 cited in the application see page 2, line 1 - page 6, line 2 ---	1,4,6
A	US,A,4 276 179 (SOEHNGEN) 30 June 1981 see column 2, line 45 - column 5, line 2 see column 13, line 63 - column 15, line 25 ---	1,2,7-11
A	FR,A,2 251 525 (COMP. FR. DE RAFFINAGE) 13 June 1975 see page 12-13; claims 1-16 ---	1,7,10, 11
A	DE,A,36 32 360 (BÖSLING) 31 March 1988 see column 1; claims 1-9 see column 3, line 49 - column 4, line 7 ---	1,5,6
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex

* Special categories of cited documents:

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Date of the actual completion of the international search

26 October 1993

Date of mailing of the international search report

05.11.93

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 93/02029

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 115 425 (AKZO) 7 September 1983 cited in the application see page 9-10; claims 1-23 ---	12
A	EP,A,0 106 970 (AM. CYANAMID CO.) 2 May 1984 ---	
A	EP,A,0 248 429 (PASSAVANT-WERKE) 9 December 1987 -----	

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

/EP 93/02029

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
NL-A-7701328	15-08-77	FR-A- 2340910	09-09-77
		BE-A- 851080	04-08-77
		DE-A- 2704569	18-08-77
		GB-A- 1535481	13-12-78
		JP-A- 52098676	18-08-77

US-A-4276179	30-06-81	CA-A- 1135680	16-11-82

FR-A-2251525	13-06-75	NONE	

DE-A-3632360	31-03-88	NONE	

GB-A-2115425	07-09-83	DE-A- 3205289	25-08-83
		CA-A- 1231210	12-01-88
		FR-A, B 2521572	19-08-83
		JP-A- 58164622	29-09-83
		SE-B- 449368	27-04-87
		SE-A- 8300766	16-08-83
		US-A- 4594207	10-06-86

EP-A-0106970	02-05-84	US-A- 4470909	11-09-84
		AU-A- 1976883	05-04-84
		CA-A- 1219881	31-03-87
		JP-A- 59082989	14-05-84
		CA-A- 1196621	12-11-85

EP-A-0248429	09-12-87	DE-A- 3618698	10-12-87
		DE-A- 3784968	29-04-93
		EP-A- 0457359	21-11-91
		US-A- 4842745	27-06-89

PATENT COOPERATION TREATY

PCT

RECEIVED

23 MAART 1994

From the INTERNATIONAL BUREAU

To:

Route

Case no.

Also Nobel Patent Department

SCHALLER, C.

Arnhem

Patent Department (Dept. APTA)

P.O. Box 9300

NL-6800 SB Arnhem

PAYS-BAS

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing:

16 March 1994 (16.03.94)

Applicant's or agent's file reference:

AFP 2318 WO

IMPORTANT INFORMATION

International application No.:

PCT/EP93/02029

International filing date:

29 July 1993 (29.07.93)

Priority date:

07 August 1992 (07.08.92)

Applicant:

AKZO N.V.

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Office of its election:

AU, CA, CZ, EP*, FI, HU, JP, KR, NO, PL, RU, US

* AT, BE, DE, DK, FR, GB, IE, IT, LU, MC, NL, PT, SE

The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of the annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent including, where applicable CH & LI, ES and GR, which cannot be elected since they are not bound by Chapter II.

With respect to Poland, a translation into Polish must always be furnished within 20 months from the priority date where those 20 months expire before 1 March 1994, even if Poland was elected for international preliminary examination before the expiration of 19 months from the priority date. Where those 20 months expire on or after 1 March 1994, the translation into Polish must be furnished, if Poland was elected for international preliminary examination before the expiration of 19 months from the priority date, before the expiration of 30 months from the priority date.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer:

J. D. Hawkins

Telephone No.: (41-22) 730.91.11

14 1-5-6

Patent Cooperation Treaty

16 NOV 1994

RMF/FFS/bz/hon

PCT

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

NOTIFICATION OF TRANSMITTAL OF
INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

To:

Mr P.C. Schalwijk
AKZO N.V.
Patent Department (Dept. APTA)
Postbus 9300
Velperweg 76
NL-6800 SB Arnhem
PAYS-BAS

Date of mailing
(day/month/year)

14. 11. 94

Applicant's or agent's file reference
AFP 2318 WO

IMPORTANT NOTIFICATION

International application No.
PCT/EP 93/ 02029

International filing date (day/month/year)
29/07/1993

Priority date (day/month/year)
07/08/1992

Applicant

AKZO NOBEL N.V. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER
The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer

[Signature]

J. Hell

I TENT COOPERATION TREAT


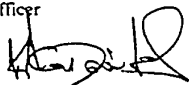
PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AFP 2318 WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP 93/ 02029	International filing date (day/month/year) 29/07/1993	Priority date (day/month/year) 07/08/1992
International Patent Classification (IPC) or national classification and IPC B01D15/00		
Applicant AKZO NOBEL N.V. et al.		

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>5</u> sheets.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings amended during international preliminary examination and/or containing rectifications made before this Authority.</p> <p>These annexes consists of a total of <u>6</u> sheets.</p>	
<p>3. This report contains indications and corresponding pages relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 	

Date of submission of the demand 10/02/1994	Date of completion of this report 14. 11. 94
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4463	Authorized officer  K. Katsoulas

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Intern. application No.

PCT/EP93/02029

I. Basis of the report

1. This report has been drawn up on the basis of:

☐ the international application as originally filed.

☒ the description, pages 6-11 _____, as originally filed,
pages _____, filed with the demand,
pages 1-5 _____, filed with the letter of 18.07.94,
pages _____, filed with the letter of _____.

☒ the claims, No. _____, as originally filed,
No. _____, as amended under Article 19,
No. _____, filed with the demand,
No. 1-6 _____, filed with the letter of 18.07.94,
No. _____, filed with the letter of _____.

☐ the drawings, sheets/fig _____, as originally filed,
sheets/fig _____, filed with the demand,
sheets/fig _____, filed with the letter of _____,
sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of: pages: _____
sheets of drawings/figures No.: _____.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed:

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Intern. application No.
PCT/EP93/02029

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability;
citations and explanations supporting such statement

1. STATEMENT

Novelty (N)	Claims 1-6	YES
	Claims	NO
Inventive Step (IS)	Claims 1-6	YES
	Claims	NO
Industrial Applicability (IA)	Claims 1-6	YES
	Claims	NO

2. CITATIONS AND EXPLANATIONS

1. D1 (US-A-4276179), which is considered as the closest prior art, discloses (column 4, column 13 line 33 to column 14 line 45) the use of a porous polyolefinic adsorbent for removing chlorinated hydrocarbons from an aqueous solution, said adsorbent being impregnated with an organic solvent (glyceryl ester) and having an average pore diameter from 0.01 to 2 μm . It follows that claim 1 differs from D1 by :
 - (a) the organic solvent is immobilised in the polymer;
 - (b) the porous polymer is regenerative;
 - (c) the particle diameter is in the range of 0.1 to 10 mm;
 - (d) the polymer/immobilised structure is obtained by heating the polymer-solvent solution at a temperature above T_c and cooling.
2. D2 (GB-A-2115425) discloses a porous polymeric structure, which is obtained by the method of feature (d) above (claim 1, page 2 lines 9-31, page 5 lines 32-55). By adjusting the ratio of solvents A and B, an adjustable pore size and wall thickness is obtained. Either or

both of components A and B can be left, immobilised (feature (a)), in the final structure. There is no mention of using the polymer/solvent structure for extraction of hydrophobic constituents from an aqueous solution. Thus, no regeneration of the structure (feature (b)) is required.

3. In D3 (US-A-4247498), a method of obtaining a similar porous structure is disclosed, wherein a porous polymer is dissolved in a compatible solvent by heating. Upon subsequent controlled cooling, a phase separation occurs. The compatible liquid can be displaced by a "useful" liquids, which can be lubricants, additives, fragrances, but not extractants. The heating temperature does not exceed T_c .
4. From the above analysis it becomes apparent that the subject-matter of claim 1 is not obvious (Art. 33(3) PCT).

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Intern. application No.
PCT/EP93/02029

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

1. According to the description, page 5 lines 9-21, the use of a mixture of solvents A and B is a prerequisite for obtaining the desired decomposition, which results in a polymer-rich and a polymer-poor phase. Thus, said hydrophobic liquid, as defined in claim 1, should be further specified (Art. 6 PCT).
2. In claim 1, the pore size range is known from D1 and consequently it belongs to the preamble of the claim.
3. In all examples I-IV, in the absence of any information concerning the polymer powder preparation with the hydrophobic substance immobilised therein (cf. page 5 and claim 1), it is not clear if by the expression polymer powder "filled" with oil, an oil immobilisation is implied (Art. 6 PCT).
4. In example V, unfilled powder is simply impregnated with xylene, by passing xylene through the column until the pores were wholly filled with xylene. It is clear that such a "filling" procedure is totally different from the claimed, i.e. heating the polymer in the solvent mixture above T_c and cooling. Thus, example V does not fall under the scope of claim 1 and should be deleted (Art. 6).
5. On page 3 lines 26-27, the wording "swelling (solid matter) or", and on page 5 line 16 the wording "if so desired", should be deleted, because they introduce ambiguity to the claims (Art. 6 PCT).

MATERIAL FOR EXTRACTING HYDROPHOBIC COMPONENTS DISSOLVED IN WATER

5 The invention relates to the use of a porous, preferably dimensionally stable, polymer for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, wherein the polymer contains a hydrophobic liquid exhibiting great affinity for the constituents to be extracted from the water and has a surface which will be wetted more readily by the hydrophobic liquid immobilised in the pores than by the aqueous solution.

10 Such a use, with a porous polymer being employed, was earlier described in US-A-4 276 179. The porous polymer used therein is obtained from olefinic materials such as polyethylene and polypropylene and possesses a rate of adsorption which is believed to be a function of the surface area which can vary from about 10 to
15 about 40 m²/g. Said surface area is achieved by providing the adsorbent with micropores having an average pore size of about 100 to about 20 000 angstroms. The porous polymer is prepared from microporous films prepared by the "dry stretch" or "solvent stretch"
20 techniques.

A major drawback of said polyolefinic films is that they cannot be regenerated by stripping with steam as they will drastically lose their adsorption efficiency, as only a few hours of heating at about
25 100°C will suffice to obtain a surface area which is far below the lower limit of 10 m²/g.

30 In GB-A-1 535 481 a porous material is employed consisting of mineral carriers which are inert with respect to water, to the hydrophobic substance to be used as extractant, and to the compound to be extracted. Examples of suitable mineral carriers mentioned are pumice, kieselguhr, bauxite, alumina, carbon, or silicates. The particles preferably have a size in the range of 0,1 mm to 5 cm. It is stated

that the pore size is critical only to the extent that it should be large enough to permit penetration of the compound to be extracted, of the extraction solvent, and of the regeneration liquid.

5 In actual practice, using the known materials for the aforementioned extraction process is attended with major drawbacks because the hydrophobic substances absorbed in them are easily displaced by water, especially when a packed bed is employed. In consequence, the water to
10 be extracted or purified is in fact contaminated rather than decontaminated by these substances.

The invention now provides for the use of a porous polymer with a hydrophobic liquid contained therein which may be regenerated and, a
15 significant increase in the capacity per volume unit notwithstanding, does not give rise to stability problems, not even when utilised on an industrial scale.

The invention consists in that for the porous polymer of the known
20 type mentioned in the opening paragraph use is made of a regenerative granulate or powder of a porous polymer having an average particle diameter in the range of 0,1 to 10 mm and pores in the range of 0,1 to 50 μ m, which is obtained by the dissolving of a polymer, with heating,
25 at a temperature above the upper critical decomposition temperature T_c in the hydrophobic liquid, followed by lowering of the temperature, resulting in a porous polymer filled with the hydrophobic substance, and the mechanical diminution of the solidified mass.

To determine the average pore diameter advantageous use is made of
30 mercury porosimetry in accordance with ASTM D 4248-83.

It is to be considered extremely surprising that by the use of a porous material having a hydrophobic surface as well as an average pore diameter within the given range both the stability and the

extraction capacity are so enhanced that now, for the first time, application on an industrial scale has become feasible.

It was found that, in general, optimum results can be obtained when using a material having an average pore diameter in the range of 0,2 to 15 μm .

The immobilised material is a liquid having the greatest possible affinity for the hydrophobic constituents to be extracted. Needless to say, this liquid should be virtually insoluble in the aqueous solution to be extracted and be so immobilised in the porous material that it cannot flow from the porous structure.

Within the framework of the invention preference is given to the use of a liquid in the form of a glycerol ester of one or more, preferably unsaturated, fatty acids.

In general, favourable results are attained if the immobilised liquid is an oil, such as palmitic oil, olive oil, peanut oil, paraffinic oil, fish oil such as herring oil, linseed oil, and, in particular, soybean oil and/or castor oil.

Generally, favourable results are attained when using a material of which at least 15 vol.% of the pores is filled with the substance immobilised therein, with optimum results being obtained using a material of which at least 50 vol.% and not more than 95 vol.% of the pores is filled with the substance immobilised therein. Completely filled up pores may cause problems on account of swelling (solid matter) or expansion (liquid), which may lead to the dimensions of the porous material being interfered with or to the immobilised liquid bursting the pores. In the case of porous materials wholly filled up with a liquid hydrophobic substance being used, these difficulties can easily be overcome by mixing the filled material with unfilled (porous) material, so that the generated excess can be absorbed during extraction. Alternatively, when a packed bed is used, the unfilled

(porous) material may be deposited at the two ends of the bed as separate boundary layers. When these types of steps are taken, 100 vol.-%-filled materials may also be employed.

5 The porous polymer is obtained by a process disclosed in US Patent Specification 4 247 498.

Examples of polymers deemed more or less suitable for use in the present invention include:

10 low pressure polyethylene, high pressure polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene terpolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(4-methyl-pentene-1), and polybutene.

15 Optimum results were attained by employing polyolefin based polymers, with preference being given to the use of a polypropylene based porous material.

20 The porous polymer is in the form of a granulate or a powder having an average particle diameter of 0,1 to 10 mm and may be used in a packed bed, a fluidised bed, or a tank with stirring.

25 Particularly when a glycerol ester of one or more unsaturated fatty acids is employed to extract aromatic compounds from aqueous solutions, preference is given to a porous material obtained by a process such as described in DE-A-32 05 289. By this process a structure may be obtained which has pores of an average diameter in the range of 0,1 to 50 μm . Especially favourable results may be obtained when using polypropylene as porous material and soybean oil/castor oil as hydrophobic substance.

30 Needless to say, the materials according to the invention are not just suitable for extracting aromatic waste matter from aqueous solutions; extracting useful constituents such as biologically active

constituents from usually highly dilute aqueous solutions is also within the bounds of possibility.

5 Generally, the procedure used to prepare the extracting material according to the invention is as follows: first, 5-90 wt.% of a polymer is dissolved, with heating, at a temperature above the upper critical decomposition temperature T_c in 10-95 wt.% of a mixture of two liquid and miscible compounds A and B, the mixing ratio of A to B being so selected as to give decomposition on cooling, resulting in a polymer-rich and a polymer-poor phase. On further lowering of the
10 temperature this decomposition structure is then fixed prior to the completion of the phase separation, due to vitrification or crystallisation of the polymer, resulting in a porous polymer material filled with the mixture of compounds A and B which is pre-eminently
15 suited to be used within the framework of the invention, either as such or after diminution if so desired.

20 The invention will be illustrated with reference to the following examples, which, of course, are not to be construed as limiting in any manner the scope of the invention.

25

30

AMENDED SHEET

CLAIMS

1. Use of a porous, preferably dimensionally stable, polymer for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, wherein the polymer contains a hydrophobic liquid exhibiting great affinity for the constituents to be extracted from the water and has a surface which will be wetted more readily by the hydrophobic liquid immobilised in the pores than by the aqueous solution, characterised in that use is made of a regenerative granulate or powder of a porous polymer having an average particle diameter in the range of 0,1 to 10 mm and pores in the range of 0,1 to 50 μm , which is obtained by the dissolving of a polymer, with heating, at a temperature above the upper critical decomposition temperature T_c in the hydrophobic liquid, followed by lowering of the temperature, resulting in a porous polymer filled with the hydrophobic liquid, and the mechanical diminution of the solidified mass.
2. Use according to claim 1, characterised in that the average pore diameter is in the range of 0,2 to 15 μm .
3. Use according to claim 1, characterised in that the hydrophobic liquid is a glycerol ester of one or more, preferably unsaturated, fatty acids.
4. Use according to claim 3, characterised in that the glycerol ester is soybean oil and/or castor oil.
5. Use according to claim 1, characterised in that the porous polymer is a polyolefin.
6. Use according to claim 1, characterised in that the porous polymer is polypropylene.

FORM PTO-1390
(REV 10-90)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

AFP2318

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 C.F.R.1.5)

INTERNATIONAL APPLICATION NO.
PCT/EP93/02029

INTERNATIONAL FILING DATE
29 July 1993

PRIORITY DATE CLAIMED
07 August 1992

TITLE OF INVENTION

MATERIAL FOR EXTRACTING HYDROPHOBIC COMPONENTS DISSOLVED IN WATER

APPLICANT(S) FOR DO/EO/US

Frederik Albert Buijtenhuijs, Johanne Josef Pragt and Elwin Schomaker

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (**unsigned**)
 10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). **Form PCT/IPEA/416 dated 14 November 1994**
- Items 11. to 16. below concern document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☐ Other items or information:

Express Mail Label No.: EG139574348US

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)		INTERNATIONAL APPLICATION NO. PCT/EP93/02029		ATTORNEY'S DOCKET NUMBER AFP2318	
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):					
Search Report has been prepared by the EPO or JPO..... \$850.00					
International preliminary examination fee paid to USPTO (37 CFR 1.482)..... \$660.00					
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).. \$730.00					
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$980.00					
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$92.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 850.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ --	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	7 -20 =	--	X \$22.00	\$ --	
Independent claims	1 -3 =		X \$76.00	\$ --	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$240.00	\$ --	
TOTAL OF ABOVE CALCULATIONS =				\$ 850.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$ --	
SUBTOTAL =				\$ 850.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ --	
TOTAL NATIONAL FEE =				\$ 850.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ --	
TOTAL FEES ENCLOSED =				\$ 850.00	
				Amount to be: refunded \$	
				charged \$	
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.					
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 01-1350 in the amount of \$ 850.00 to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-1350. A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Mr. Joseph M. Noto Akzo Nobel Inc. Patent and Trademark Department 7 Livingston Avenue				SIGNATURE Joseph M. Noto NAME 32,163 REGISTRATION NUMBER	



UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

08/381828
US APPLICATION NO. 5611 FIRST NAMED APPLICANT TENHUIJS F AFF2318 ATTY. DOCKET NO.

MR. JOSEPH M. NOTO
AKZO NOBEL INC.
PATENT & TRADEMARK DEPT.
7 LIVINGSTONE AVENUE
DOBBS FERRY, NY 10522

5611
RECEIVED
AKZO NOBEL INC.
APR 13 1995

PCT/EP93/02029
INTERNATIONAL APPLICATION NO.

07/29/93 08/07/92
I.A. FILING DATE PRIORITY DATE
04/11/95

PATENT & TRADEMARK DEPT.
DOBBS FERRY
DATE MAILED:

NOTIFICATION OF ACCEPTANCE OF APPLICATION UNDER 35 U.S.C. 371
AND 37 CFR 1.494 OR 1.495

1. The applicant is hereby advised that the United States Patent and Trademark Office in its capacity as
☐ a Designated Office (37 CFR 1.494), ☒ an Elected Office (37 CFR 1.495), has determined
that the above identified international application has met the requirements of 35 U.S.C. 371, and is
ACCEPTED for national patentability examination in the United States Patent and Trademark Office.

2. The United States Application Number assigned to the application is shown above and the relevant
dates are:

16 Mar 1995 16 Mar 1995
35 U.S.C. 102(e) DATE DATE OF RECEIPT OF
35 U.S.C. 371 REQUIREMENTS

3. ☒ A request for immediate examination under 35 U.S.C. 371(f) was received on 07 Feb 1995
and the application will be examined in turn.

4. The following items have been received:

- ☒ U.S. Basic National Fee.
- ☒ Copy of the international application in:
 - ☐ a non-English language.
 - ☒ English.
- ☒ Translation of the international application into English.
- ☒ Oath or Declaration of inventor(s) for DO/EO/US.
- ☐ Copy of Article 19 amendments. ☐ Translation of Article 19 amendments into English.
The Article 19 amendments ☐ have ☐ have not been entered.
- ☒ The International Preliminary Examination Report in English and its Annexes, if any.
- ☒ Translation of Annexes to the International Preliminary Examination Report into English.
The Annexes ☒ have ☐ have not been entered.
- ☒ Preliminary amendment(s) filed 07 Feb 1995 and _____
- ☐ Information Disclosure Statement(s) filed _____ and _____
- ☐ Assignment document.
- ☐ Power of Attorney and/or Change of Address.
- ☐ Substitute specification filed _____
- ☐ Verified Statement Claiming Small Entity Status.
- ☒ Priority Document.
- ☒ Copy of the Search Report ☒ and copies of the references cited therein.
- ☐ Other:

A Filing Receipt (PTO-103X) will be issued for the present application in due course. Once the
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